PFBC ASH UTILIZATION

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ABSTRACT

Pilot-scale development at Foster Wheeler Energia Oy 10 MW_{th} circulating PFBC at Karhula, Finland, have demonstrated the advantages of pressurized fluidized bed combustion (PFBC) technology. Commercial scale deployment of the technology at the Lakeland Utilities MacIntosh Unit No. 4 has been proposed. Development of uses for the ashes from PFBC systems is being actively pursued as part of commercial demonstration of PFBC technologies.

Western Research Institute (WRI), in conjunction with the U.S. Department of Energy (DOE), Federal Energy Technology Center (FETC), Foster Wheeler Energy International, Inc. and the Electric Power Research Institute (EPRI), conducted a laboratory scale investigation of the technical feasibility of PFBC ash as a (1) material for use in construction applications and (2) amendment for acidic problem soils and spoils encountered in agricultural and reclamation applications. Ashes were collected from the Foster Wheeler Energia Oy pilot circulating PFBC tests in Karhula, Finland, operating on (1) low-sulfur subbituminous and (2) high-sulfur bituminous coals.

PFBC Ash Use In Construction Applications

The technical feasibility study examined the use of PFBC ash in construction-related applications, including its use as a cementing material in concrete and use in cement manufacturing, fill and embankment materials, soil stabilization agent, and use in synthetic aggregate production. The results of the technical feasibility testing indicated the following:

- PFBC ash does not meet the chemical requirements as a pozzolan for cement replacement. However, it does appear that potential may exist for its use in cement production as a pozzolan and/or as a set retardant.
- PFBC ash shows relatively high strength development, low expansion, and low permeability properties that make its use in fills and embankments promising.
- Testing has also indicated that PFBC ash, when mixed with low amounts of lime, develops high strengths, suitable for soil stabilization applications and synthetic aggregate production. Synthetic aggregate produced from PFBC ash is capable of meeting

American Society for Testing Materials (ASTM and American Association of State Highway Transportation Officials (AASHTO) specifications for many construction applications.

In summary, PFBC ash represents a viable material for use in currently established construction applications for conventional coal combustion ashes.

PFBC Ash as a Soil/Mine Spoil Amendment

The technical feasibility study examined the technical feasibility of PFBC ash as a soil amendment for acidic problem soils and spoils encountered in agricultural and reclamation applications. The results of the technical feasibility testing indicated the following:

- PFBC fly ashes were effective acid soil and mine spoil amendments. In a comparison with ag-lime, the Karhula fly ashes reacted with the acidic spoil at a slower rate and the final pH of the treated material was slightly lower (i.e., fly ash treated, pH ≅ 7 and the ag-lime treated ≅ 8). Electrical conductivity (EC) values of the fly ash treated spoils were approximately 1 mS/cm higher than the EC values associated with the ag-lime treated materials.
- The greenhouse study demonstrated that PFBC fly ash and/or bed ash amended spoils resulted in higher seed germination than the ag-lime amended spoils. These results were possibly due to pH and nutritional issues.
- The greenhouse study also demonstrated that PFBC fly ash and/or bed ash amended spoils resulted in comparable plant productivity to the ag-lime amended spoils. These results were also due to pH and nutritional issues, but root penetration was undoubtedly also a factor.

In summary, PFBC ash represents a viable material for use in currently established mining and soil amendment applications.

Conclusions

In conclusion, there is a significant market potential for PFBC ash in the construction and soil amendment industries. PFBC ash should be viewed as a valuable resource, and commercial opportunities for these materials should be explored for future PFBC installations.

INTRODUCTION

Pressurized fluidized bed combustion (PFBC) represents one of the most promising emerging Clean Coal Technologies (CCT). PFBC has been demonstrated at near commercial scale at the American Electric Power (AEP) Tidd bubbling PFBC demonstration plant in Ohio, as well as at Vartan in Sweden and Escatron in Spain. Circulating PFBC technology is being demonstrated at the pilot-scale at Foster Wheeler Energia Oy in Karhula, Finland.

The utilization of ash from fluidized bed combustion (FBC) units is a promising ash management option. The chemical characteristics of pressurized fluidized bed combustion ash compared to other FBC ashes have generated interest in the use of PFBC ash for various construction and agricultural applications. However, before commercial entities are ready to commit to the concept of using PFBC ash, its performance in viable applications must be documented.

Western Research Institute (WRI) has completed a three-year project under sponsorship of the Electric Power Research Institute (EPRI), Foster Wheeler Energy International, Inc., and the U.S. Department of Energy (DOE) Federal Energy Technology Center (FETC) that addressed ash use markets and options for PFBC technologies.

The overall objectives of this study were to determine the market potential and the technical feasibility of using PFBC ash in high-volume use applications. The study was of direct use to the utility industry in assessing the economics of

PFBC power generation, particularly in light of ash disposal avoidance achieved through ash use. Additional benefits can be realized by a utility through CO_2 offset credits resulting from ash penetration into certain markets that generate high levels of greenhouse gases during manufacturing (e.g., cement production).

The specific objectives of the program were:

- to define present and future market potential of PFBC ash for a range of applications;
- to assess the technical feasibility of PFBC ash use in construction and soil/spoil amendment applications; and
- to demonstrate the most promising of the ash use options in full-scale field demonstrations.

This paper addresses the results of the technical feasibility of ash use options for PFBC units using low-sulfur and high-sulfur coal and limestone sorbent-derived ashes (Karhula-low ashes and Karhula-high ashes).

ASH SOURCES AND CHARACTERISTICS

Ash Sources

The study of PFBC ash use options has included three different ashes: (1) ash from the Foster Wheeler Energia Oy circulating PFBC pilot plant in Karhula Finland, burning low-sulfur subbituminous coal; (2) ash from the Foster Wheeler Energia Oy circulating PFBC pilot plant in Karhula, Finland, burning high-sulfur bituminous coal. Two sets of fly ash and bed ash from the Foster Wheeler Energia Oy pilot-scale circulating PFBC unit in Karhula, Finland, represented the combustion of low-sulfur Powder River Basin subbituminous coal (Black Thunder) with limestone sorbent and the combustion of high-sulfur Illinois Basin coal with a limestone sorbent.

General Chemistry of As-Received PFBC Ashes

Major element chemistry of the fly ash and bed ash from each of the PFBC sources was determined by X-ray fluorescence, using standard calibration curves. Phase identification of the fly ashes and bed ashes was determined by X-ray diffraction (XRD), wet chemical methods described by American Society for Testing and Materials (ASTM) C-25, and methods described by Iribarne (1993). Leachate characteristics of the ashes were tested according to the U.S. EPA Toxicity Characteristics Leaching Procedure (TCLP) (EPA CFR Part 241).

The chemical compositions of the Karhula ashes are presented in Table 1. The loss on ignition (LOI) is composed of the moisture and the organic carbon. The LOI in the PFBC ashes has been corrected for mineral carbon. Moistures are less than 0.1% and the organic carbon contents are less than 2%. The free lime (CaO) content of the PFBC ashes was determined by ASTM C-25 to be in the range of 0.5 to 1.0%. The majority of the lime appears to still be carbonated in the form of $CaCO_3$. With the exception of relatively high mineral carbon, the chemistry of the PFBC ashes is typical of ashes from FBC of low-sulfur and high-sulfur coals using limestone and dolomite sorbents. The chemical compositions of the Karhula ashes have been presented in Bland et al., (1995a, 1997c).

Phase analyses of the ashes by X-ray diffraction are presented in Figure 1. The Karhula ashes are composed principally of anhydrite ($CaSO_4$), calcite ($CaCO_3$), coal ash oxides, and dehydroxylated clays. The lack of lime (CaO) in the PFBC ashes is distinctly different from AFBC ashes, which contain large amounts of lime. In PFBC systems, the partial pressure of CO_2 favors both calcination and recarbonization. This results in low lime and high carbonates (calcite) in pressurized FBC ash.

Table 1. Chemical Composition of the PFBC Ashes

Chemical Parameter, wt. %	Karhula-Low (1) Fly Ash	Karhula-Low (1) Bed Ash	Karhula-High (2) Fly Ash	Karhula-High (2) Bed Ash
SiO_2	37.84	47.02	29.46	6.15
TiO_2	0.87	0.40	0.43	0.12
Al_2O_3	14.27	14.57	12.48	4.20
Fe_2O_3	4.95	3.80	8.69	1.33
CaO	21.61	16.13	23.50	42.68
MgO	3.07	2.23	0.84	0.52
K_2O	0.97	2.09	1.27	0.05
Na_2O	1.55	2.37	1.07	0.51
P_2O_5	0.76	0.50	0.50	0.95
SO_3	12.17	9.39	20.83	23.56
CO_2	0.55	1.77	0.56	18.85
LOI*	0.26	0.31	0.26	0.98
Total	99.37	99.76	99.89	99.70

(1) Karhula-low are ashes from the combustion of low-sulfur subbituminous coal in Karhula facility
(2) Karhula-high are ashes from the combustion of high-sulfur bituminous coal in Karhula facility
* LOI corrected for carbonate losses

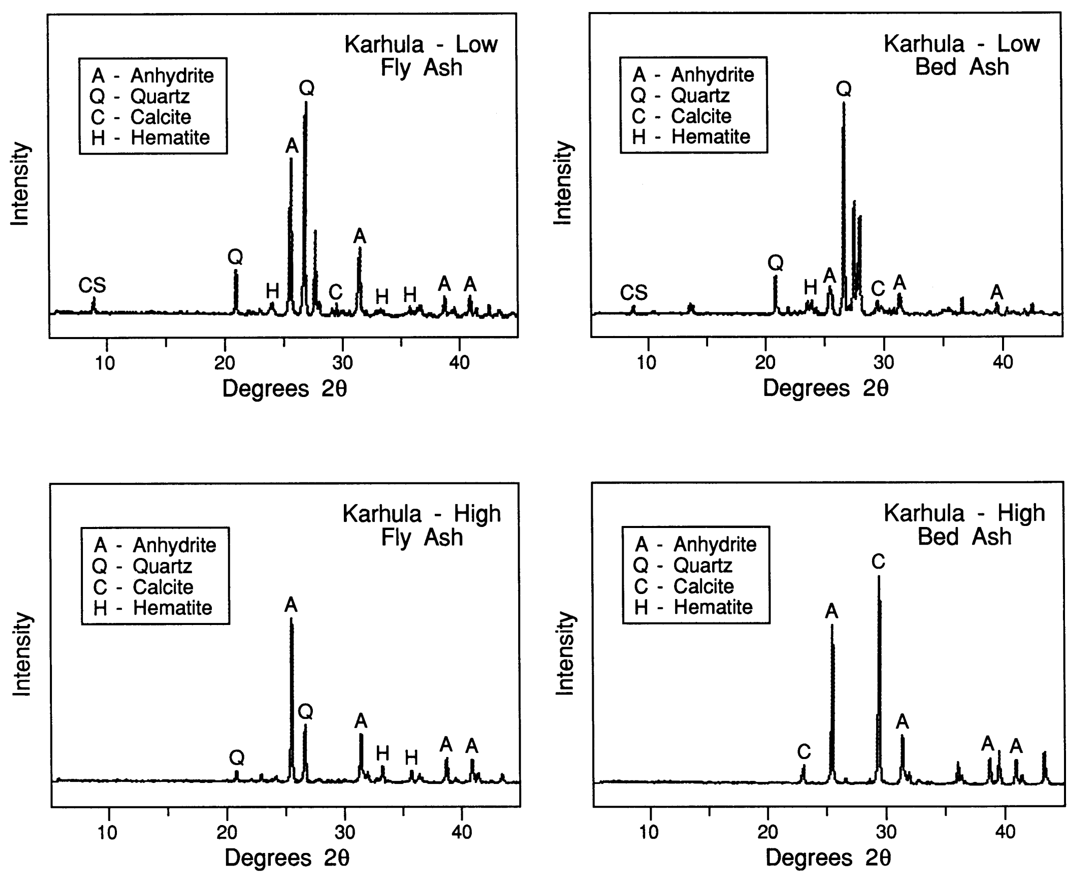


Figure 1. X-ray Diffractograms of the PFBC Fly Ashes and Bed Ashes (a) Karhula-Low and (b) Karhula-High

Table 2. Summary of the TCLP Leachate Analysis for PFBC Ashes

Chemical Parameter	Regulatory Limit, mg/L	Karhula-Low		Karhula-High	
		Fly Ash	Bed Ash	Fly Ash	Bed Ash
Arsenic (As)	5.0	0.041	<0.04	<0.04	<0.04
Barium (Ba)	100	0.395	0.241	0.26	0.32
Cadmium (Cd)	1.0	<0.01	<0.01	<0.01	<0.01
Chromium (Cr)	5.0	<0.05	<0.05	0.12	<0.05
Lead (Pb)	5.0	<0.1	<0.1	<0.1	<0.1
Mercury (Hg)	0.2	<0.002	<0.002	<0.002	<0.002
Selenium (Se)	1.0	<0.2	<0.2	<0.2	<0.2
Silver (Ag)	5.0	<0.01	<0.01	<0.01	<0.01
pH	na	9.2	8.0	9.39	9.60

na - not applicable

The chemical characteristics of the leachates generated by the TCLP, were also determined for the bed ash and fly ash from the Karhula-low and Karhula-high ash sources. These data are presented in Table 2. The data substantiate that none of the leachates generated from the PFBC ashes exceeded the 1976 Resource Conservation and Recovery Act (RCRA) limits. As such, these ashes would **NOT** be classified as hazardous. Ashes from other coal-fired power systems are already categorized as nonhazardous and have been given an exclusion from these RCRA requirements.

Physical Properties of PFBC Ashes

The general physical properties of the ashes were also determined, including bulk densities, specific gravity, and particle size distribution. The bulk density and specific gravities of the as-received ashes are presented in Table 3.

The bulk densities of the Karhula-low and Karhula-high fly ashes and bed ashes were determined according to ASTM procedures.

The size distribution is similar to that of other FBC ashes reported in the literature (Georgiou et al., 1993; Bland et al., 1993b; Bigham et al., 1993).

PFBC ASH USE IN CONSTRUCTION APPLICATIONS

Laboratory and pilot-scale tests were conducted to address the use of Karhula PFBC ash in a number of construction applications, including (1) cement replacement and cement manufacturing, (2) fills and embankment construction, (3) soil stabilization applications, and (4) synthetic aggregate production.

Table 3. Summary of the Bulk Densities and Specific Gravities of the PFBC Ashes

Physical Properties	Minimum (Poured) Bulk Density, kg/m3 (pcf)	Maximum (Packed) Bulk Density, kg/m3 (pcf)	Specific Gravity g/cc
Karhula-Low			
Fly Ash	948 (59.2)	1162 (72.5)	2.34
Bed Ash	1368 (85.4)	1528 (95.4)	2.55
Karhula-High			
Fly Ash	795 (49.6)	1051 (65.6)	2.73
Bed Ash	1289 (80.5)	1397 (87.2)	2.81

Table 4. ASTM C-311 Test Results for PFBC Fly Ashes

	Karhula Low Fly Ash	Karhula High Fly Ash	ASTM C-618 Specifications	
			Class F	Class C
Chemical Properties				
$SiO_2+Al_2O_3+Fe_2O_3$, wt.%	57.57	50.63	70 min	50 min
Sulfur Trioxide, wt.%	12.17	20.83	5 max	5 max
Moisture Content, wt. %	0.09	0.15	3 max	3 max
Loss on Ignition, wt. %	0.81	0.82	6 max	6 max
Available Alkalis, wt.%	0.70	1.16	1.5 max	1.5 max
Physical Properties				
Fineness, % retained 325 mesh	25.58	37.83	34 max	34 max
Pozzolanic Activity Index				
With PC*, % of control @ 28 days	83.4	59.4	75 min	75 min
Water Requirement, % of control	97.7	102.5	105 max	105 max
Soundness - Autoclave Expansion, %	-0.040	-0.059	0.8 max	0.8 max
Drying Shrinkage Increase @ 28 d, %	0.016	0.027	0.03 max	0.03 max

*PC - portland cement

PFBC Ash Use in Concrete and Cement Production

PFBC ash may be used in concrete and in cement production (1) as a replacement of cement in portland cement concrete; (2) as a pozzolanic material in the production of pozzolanic cements (e.g., Type IP); and (3) as a set retardant interground with cement as a replacement for gypsum.

Cement Replacement The use of PFBC ash as a pozzolan for replacement of portland cement in concrete products is dependent on the results of the ASTM C-311 testing and the specifications of ASTM C-618. The Karhula fly ashes were tested according to ASTM 311 and the results are presented in Table 4.

The data indicate that the ashes do not qualify as pozzolans according to ASTM C-311 because the sulfate levels exceed the ASTM C-618 specification of 5% maximum SO_3 content. This will restrict the use of certain PFBC ashes as pozzolans for portland cement applications.

Portland Cement Production PFBC ash can be incorporated into the cement manufacturing process as an ingredient in the clinker production and secondly as an interground material in the production of Type IP pozzolanic cements. Type IP cement is a pozzolan portland cement commonly used for general construction applications.

The characteristics of the ash for these applications are defined under ASTM C-595 and C-593. The use of ash as a pozzolan in blended cement according to ASTM C-595 does not rely on the chemical properties of the pozzolan and instead is based on performance specifications for the resultant blended cement. Calculations related to the potential use of the PFBC ashes in the manufacturing of blended Type IP cement are presented in Table 5. It is clear that PFBC ash could be used in substantial amounts in Type IP portland cement.

PFBC Ash Use as Structural Fill and Embankment Materials

The application of PFBC residue as an engineered material for structural fills and embankments represents a large-scale use option. Structural fills and embankments are numerous in the road construction, mining, and industrial construction industries.

Table 5. Summary of Chemical Specifications for PFBC Ash Use in Type IP Cement

Chemical Requirements	Karhula -Low Fly Ash[a]	Karhula-High Fly Ash[a]	ASTM C-595 Specifications
MgO, %	2.9	2.5	5.0 Max.
SO3, %	2.9	2.9	4.0 Max.
LOI, %	1.0	1.0	5.0 Max.
Fly Ash Addition, %	23.8	13.9	-
Gypsum Required, %	-	-	-

a. Calculations are based on fly ash interground with Type I portland cement to achieve (1) equivalent of 5% gypsum addition or (2) a maximum of 4% MgO content in cement.

In addition to these typical compacted fill applications, there is potential use of PFBC ash in controlled density low-strength flowable fill (CDLSFF) applications. This material is not really concrete and is highly flowable (slump 9-10 inches). CDLSFF is usually mixed in a ready-mix concrete truck, with mixing continuing during transport to prevent segregation. The CDLSFF is discharged and placed using chutes or can be pumped using standard concrete or grout equipment. A number of applications have been documented for CDLSFF, including excavatable backfills and trench/pipe bedding, structural fills, road bases, caisson and pile fills, and mine void filling. PFBC ash is marketable in both compacted fill and flowable fill applications.

Geotechnical tests were conducted to determine the possible use of these ashes as compacted structural fill or embankment material, as well as flowable fill material for excavatable trench grade and structural fill applications. A description of the results of testing for each of these engineered fill materials is provided below.

Compacted Fills and Embankments The geotechnical tests related to compacted structural fills and embankments focused on the moisture-density relationship (Proctors), unconfined compressive strength, expansion and swell, and permeability.

Moisture-density relationships were determined using ASTM D-698 and ASTM D-1557 compactive efforts. The moisture-density results for the Karhula ash blends compacted at D-698 and D1557 compactive efforts are presented in Figure 2.

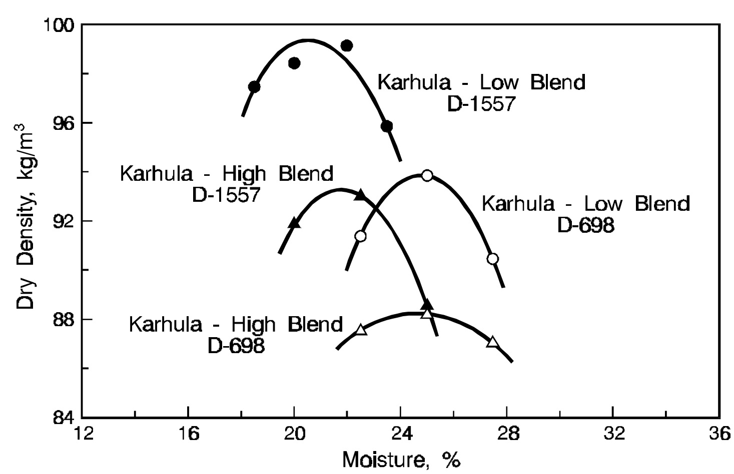


Figure 2. Moisture-Density Relationships of Karhula PFBC Ashes

The compactive effort employed in the ASTM D-1557 tests is higher than that for ASTM D-698. The compactive efforts represented by these two methods typically cover the range of compaction achievable with standard construction equipment.

The lower optimum moisture and higher maximum dry density observed for the Karhula-high ash blend are consistent with the higher specific gravity of the Karhula-high ash blend relative to the Karhula-low ash blend.The ASTM D-698 and D-1557 data are consistent with the expected behavior of different compactive efforts (i.e., lower optimum moisture and higher maximum dry density for increased compactive effort).

Testing also addressed the strength development of the two ash blends as related to their use in compacted structural fills and embankments. The ash blends are a composite of the fly ash and the bed ash in approximate proportions to those produced in the combustor. Specimens prepared at ASTM D-698 and D-1557 moistures and densities were cured under sealed conditions at 23°C.

Strength development for the Karhula ash blends under sealed conditions for different compactive efforts is presented in Figure 3. The strength development of the Karhula PFBC ashes are a factor of 4 to 10 times higher than that for other soils and fill materials.

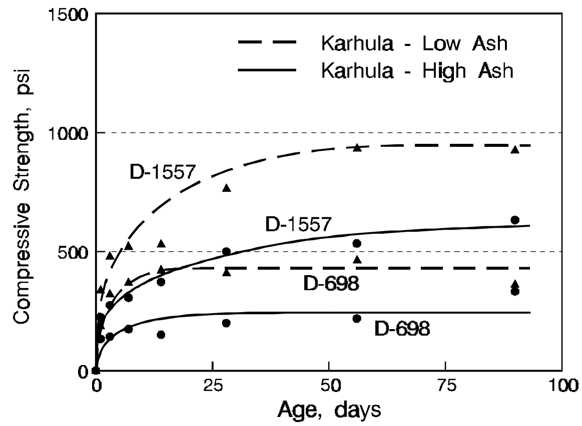


Figure 3. Strength Development of PFBC Ash Blends, Sealed Cured at 23°C.

In addition, the ASTM D-1557 compacted specimens were found to be stronger than the ASTM D-698 compacted specimens.

The strength development of PFBC ashes are related to differences in the hydration reaction chemistry of the two ashes (Bland, 1996). Strength test specimens were tested for the hydration reaction phases by X-ray diffraction. The results of this hydration reaction geochemical testing were presented by Bland and Brown (1997a). The results of the hydration reaction phase analysis by XRD for the Karhula PFBC ash blends are presented in Figure 4.

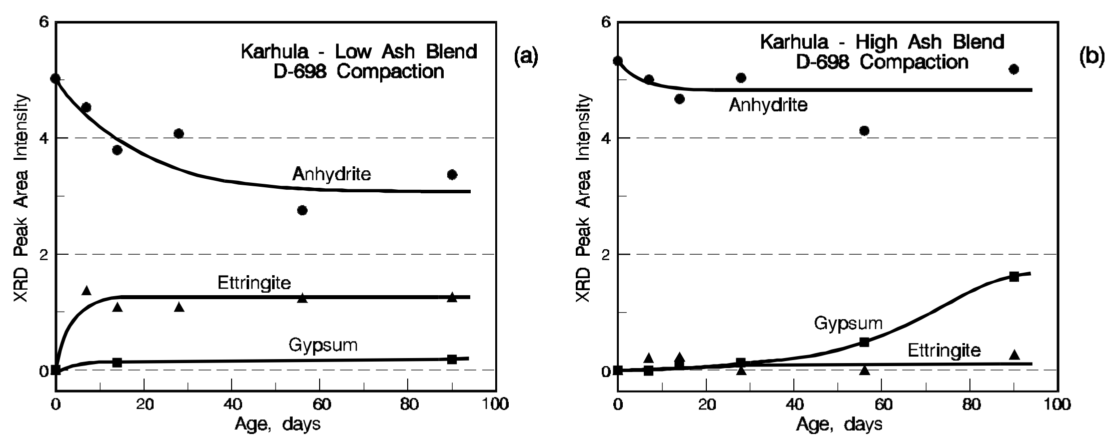


Figure 4. X-ray Diffraction Peak Area Intensities of Hydration Phases as a Function of Curing Time (a) Karhula-Low PFBC Ash Blend and (b) Karhula-High PFBC Ash Blend

Table 6. Expansion Results for ASTM D-698 and 1557 Compacted PFBC Ashes

Unconfined Linear Expansion, %	**Karhula-Low Ash Blend** Sealed	Sat. (1)	**Karhula-High Ash Blend** Sealed	Sat. (1)
D-698 Compaction				
7 days	-0.007	(3)	0.000	(3)
90 days	0.000	0.044	0.000	0.036
180 days	0.004	0.071	0.000	0.071
365 days	0.013	0.062	0.018	0.124
2 years	0.022	0.178	na	na
D-1557 Compaction				
7 days	0.000	0.009	0.009	-0.013
90 days	0.009	0.142	0.009	0.036
180 days	0.009	0.146	0.036	0.053
365 days	-0.015	0.148	na	na
2 years	0.044	0.156	na	na

na-not available

(1) Specimens submerged in ash/water slurry after 14 days sealed curing.

Figure 4 presents the XRD peak area intensities of the hydration phases present as a function of curing time. Both of the Karhula ash blends showed a decrease in anhydrite peak area with curing time and the formation of gypsum and ettringite. The Karhula-low ash forms considerably more ettringite than does the Karhula-high ash. In addition, the Karhula-high forms gypsum after approximately two months.

Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) and gypsum ($CaSO_4\cdot 2H_2O$) are the main hydration reaction products found in the PFBC ashes. Anhydrite appears to be hydrated with time, presumably forming gypsum. Gypsum ($CaSO_4\cdot 2H_2O$) forms from anhydrite ($CaSO_4$), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) forms from soluble calcium, alumina, and gypsum. These hydration reactions and reaction products have been reported for PFBC ashes (Bland et al., 1997a) and are typical of CFBC ashes (Anthony et al., 1995; Bland et al., 1997a).

The expansion properties of the conditioned and compacted Karhula ashes were determined according to modified ASTM C-157 procedures in which the expansion is essentially unrestricted. The results for the Karhula ash blends for ASTM D-698 and D-1557 compactive efforts are presented in Table 6. The results indicate that the expansion for each of the ash blends are essentially identical, with expansion of near zero percent. In addition, the ASTM D-698 and D-1557 compacted ash blend specimens cured under both sealed and saturated conditions showed essentially no expansion.

The permeabilities or hydraulic conductivities (k) of the PFBC ash blends were determined according to ASTM procedures. The ashes were compacted at ASTM D-698 and D-1557 optimum moisture and density. The results are presented in Table 7. As expected, the permeability of the PFBC ash blends continued to decrease with curing. Hydraulic conductivities in the range of 10^{-5} to 10^{-7} cm/sec were determined at early ages for the ASTM D-698 compacted ash blends and continued to decrease with time to 10^{-6} to 10^{-8} cm/sec at 28 days. These results indicate that the PFBC ashes result in a solid impermeable material ideal for many construction fill applications.

These values are typical of those reported for CFBC ashes (Georgiou, et al., 1993). The ASTM D-1557 compacted ash blends were less permeable than the D-698 compacted ash blends. Typically, the ASTM D-1557 specimens were half to an order of magnitude less permeable than the ASTM D-698.

Table 7. Hydraulic Conductivity of ASTM D-698 and D-1557 Compacted PFBC Ash

	ASTM D-698 k, cm/sec	ASTM D-1557 k, cm/sec
Karhula-Low Ash Blend (1)		
Initial	9.1 E-6	2.6 E-6
28 day	6.2 E-6	1.4 E-6
Karhula-High Ash Blend (2)		
Initial	1.1 E-5	6.0 E-6
28 day	6.0 E-6	3.9 E-6

Controlled Density Low-Strength Flowable Fills. The second fill application involves controlled density low-strength flowable fill material, which has been used in construction applications for a number of years. Controlled density low-strength flowable fill material is a mixture of cement, fly ash, sand, and water that has a specific strength dependent upon the end use. CDLSFF offers favorable economics compared to other fill materials because it requires less excavation and compaction during construction.

The results of tests using Karhula PFBC ashes in CDLSFF are represented in Table 8. Structural fill grade CDLSFF, requiring in excess of 6.89 MPa (1000 psi) strength, and excavatable trench fill grade, requiring strengths in the range of 700 to 1400 kPa (100 to 200 psi), were tested. Removability or excavatability were defined from the general requirements of <1 MPa (150psi) unconfined compressive strength for 'excavatable' grade and >6.9 MPa (1,000 psi) for 'structural' grade. The data clearly show that both the Karhula fly ashes can be used as CDLSFF.

PFBC Ash Use for Soil Stabilization

The use of PFBC ash and other FBC residues for stabilization of soils is a potentially large ash use market. This ash use application is similar to the cement stabilization of soils commonly applied in the construction industry. Soil stabilization is based on the treatment of clay soils with a material to provide strength and stability. Cement-fly ash and lime-fly ash mixtures are commonly employed at levels of 10 to 20% of the soil. FBC ashes exhibit self-cementing characteristics and, as such, have been proposed as a viable stabilizing agent.

Table 8. Summary of Properties of Flowable Fill Materials Made with PFBC Ash

	Structural Grade Fill		Excavatable Trench Grade Fill	
	Karhula-Low	**Karhula-High**	**Karhula-Low**	**Karhula-High**
Mix Components, kg/m^3				
Portland Cement	113	113	48	48
PFBC Fly Ash	267	267	267	267
Penetration Resistance, kPa				
4 hours	400	476	28	538
8 hours	2165	896	193	786
24 hours	2647	3961	883	2096
Compressive Strength, kPa				
2 days	903	524	317	138
7 days	2055	1930	579	629
28 days	7108	5481	1400	1051

na-not available

For a material to be considered as a cementing agent for soil stabilization applications, the material must show strength development, freeze/thaw durability, and wet/dry durability in compliance with ASTM D-1632, D-560, and D-559, respectively.

A viable cementing material needs to exhibit strength in the range of 27.6 Mpa (4000 psi) and durability of 12 cycles of freeze/thaw and wet/dry for the cementing material only. These requirements result from stabilized soil specifications of 2.76 MPa (400 psi) and durability to 12 cycles of wet/dry and freeze/thaw when soils are treated at 10 to 20% cementing levels.

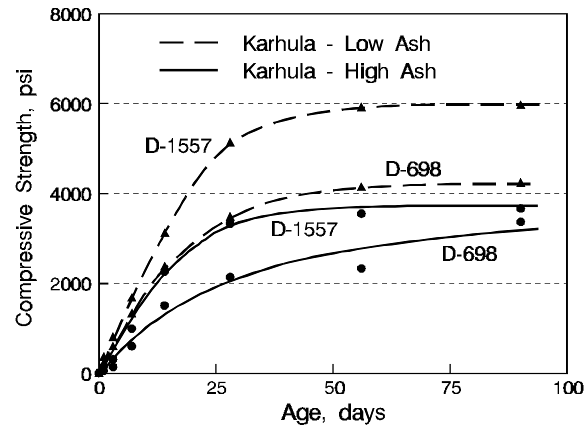
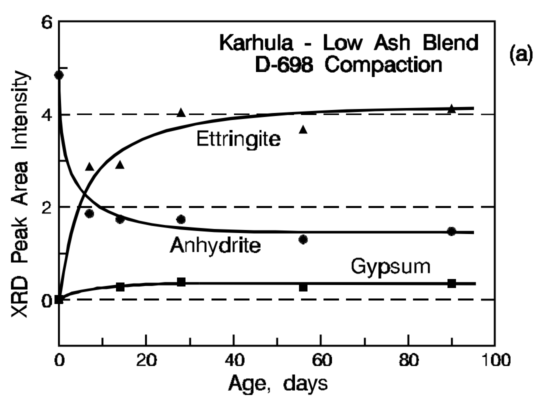


Figure 5. Strength Development of PFBC Ash Blends With Lime Enhancement

Unconfined Compressive Strength Relationship
Testing was conducted using the Karhula ash blends with and without hydrated lime addition, in order to determine their potential as a cementing agent for soil stabilization applications. Typical results of the testing are displayed in Figure 5. The results showed that the addition of 5% hydrated lime increased the strength to over 29.3 MPa (4,700 psi) at 90 days for Karhula-low D-698 compacted ash blend, and to over 23.3 MPa (3,380 psi) for Karhula-high D-698 compacted ash blend. These strengths are considerably higher than those reported for Karhula ashes without lime (Figure 3).

The strength development was found to be higher with compactive effort, as well as with lime enhancement. The low strengths of the ash blends without lime are sufficient for many applications, such as fills and embankments. However, for other applications, such as soil stabilization, lime enhancement will be required at some level (e.g., 5% or less).

As mentioned earlier, these differences in strength are due to differences in the hydration chemistry of the two ashes (Bland, 1997a). Compared with the data in Figure 4, lime addition results in an increase in the formation of ettringite in both of the Karhula ashes (Figure 6).



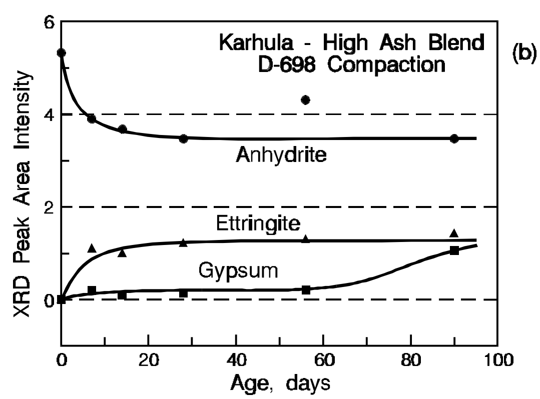


Figure 6. X-ray Diffraction Peak Area Intensities of Hydration Phases in Lime-Enhanced PFBC Ashes as a Function of Curing Time (a) Karhula Low, and (b) Karhula High PFBC Ash Blends

Table 9. Expansion Results for PFBC Ashes With and Without Lime Enhancement

Unconfined Linear Expansion, %	Karhula-Low		Karhula-High	
	Sealed Curing	Saturated Curing (1)	Sealed Curing	Saturated Curing (1)
No Lime Enhancement				
7 days	-0.007	(3)	0.000	(3)
90 days	0.000	0.044	0.000	0.036
180 days	0.004	0.071	0.000	0.071
365 days	0.013	0.062	0.018	0.124
2 years	0.022	0.178	na	na
Lime Enhancement				
7 days	0.928	(3)	0.000	(3)
90 days	1.494	1.534	0.111	0.218
180 days	1.440	1.556	0.116	0.244
365 days	1.422	1.548	0.138	0.276
2 years	1.471	1.619	na	na

na-not available

(1) Specimens submerged in ash/water slurry after 14 days sealed curing.

The ettringite formation is believed to be directly responsible for the enhanced strength development. As also noted in Figure 4, the lime-enhanced Karhula-high ash shows lower ettringite formation with an increase in gypsum formation after 2 months.

Expansion Properties The expansion properties of the conditioned and compacted Karhula ashes with and without hydrated lime addition were tested for soil stabilization applications, according to a modified ASTM C-157 procedure. Tests were conducted on ASTM D-698 and D-1557 compacted ash bars. The results for the ASTM D-698 compacted PFBC ashes with and without lime and cured under sealed and saturated conditions are shown in Table 9.

The lime-enhanced Karhula ash blend showed expansion of approximately 1.5%, while the ash blend without lime enhancement showed essentially no expansion. The expansion noted for the lime-enhanced ash appears to occur early, within the first 20 to 30 days. Although the expansion is significant, it appears controllable and manageable, and it should be possible to balance the strength and swelling properties in certain applications. For example, in certain grouting applications, such as subsidence control in underground construction operations, controlled expansion of the magnitude reported is desirable.

Freeze/Thaw and Wet/Dry Cycle Durability Conditioned and compacted Karhula ash blend specimens were subjected to 12 cycles of freeze/thaw (ASTM D-560) and wet/dry (ASTM D-559) conditions. The results (Figure 7) indicated that all of the PFBC ashes with 5% hydrated lime enhancement survived the entire 12 cycles with losses less than the 15% maximum limit. Typical losses of less than 5% were determined. The data imply that the PFBC ash makes an excellent stabilization agent with excellent durability characteristics.

PFBC Ash Use in Synthetic Aggregate Production

The aggregate market encompasses conventional aggregate products, such as masonry units and ready-mix concrete. Also, with crushing, aggregates can be produced for use in asphalt paving, road base construction, and roller compacted concrete. Lightweight aggregate can also be used in many structural building products. As such, synthetic aggregate for construction applications appears to be a major market for PFBC ashes.

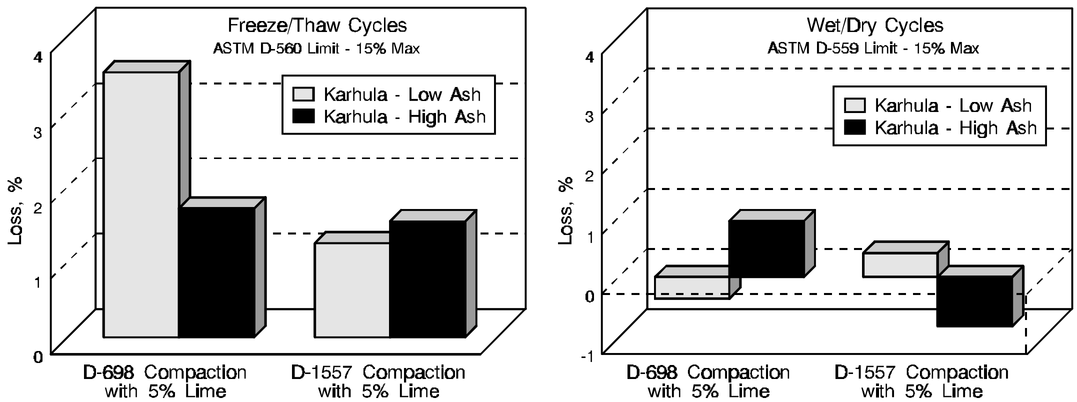


Figure 7. Freeze-Thaw and Wet-Dry Cycle Durability Results for the Karhula Ashes

Synthetic aggregate has been manufactured from power plant ash that can meet the requirements for conventional aggregate products, such as masonry units and ready-mix concrete. With crushing, synthetic aggregate can be produced for use in asphalt paving, road base construction and roller-compacted concrete.

Pelletizing Trials Pelletizing trials were conducted simulating the AET process for the pelletization of FBC ashes, as described in the literature (Bland et al., 1992, 1993a). Pelletizing trials were conducted at the WRI Waste Management Laboratory, employing a high-speed pin mixer for conditioning of the ash and a 3-foot diameter pelletizing pan for the agglomeration of the conditioned ash into a pelletized form. A schematic of the AET pelletizing process for PFBC ash is presented in Figure 8. Pelletizing trials were conducted employing Karhula ash blends with and without lime enhancement. The pelletizing addressed the water requirements and other processing parameters pertinent to defining the technical feasibility and relative economics of aggregate production from PFBC ashes.

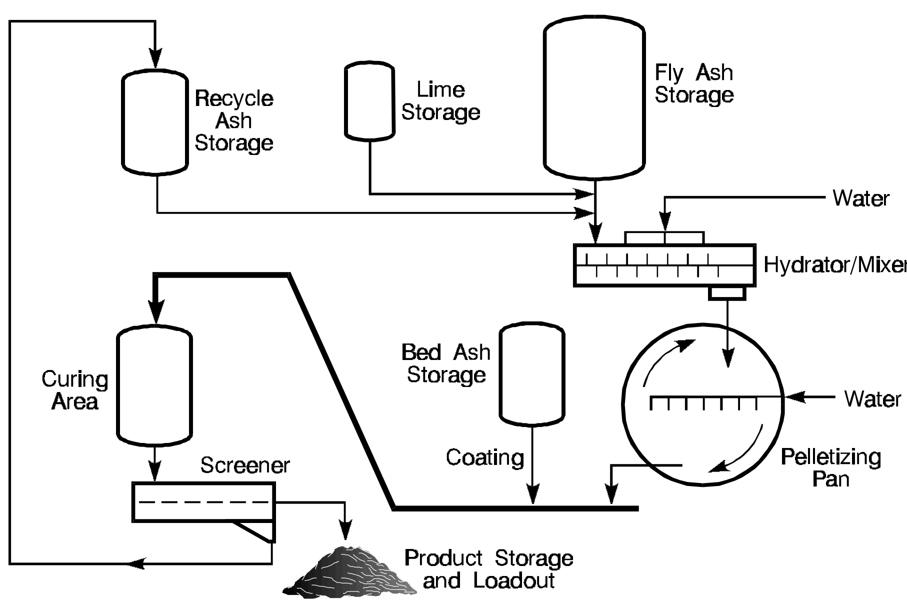


Figure 8. Schematic of the AET Synthetic Aggregate Process for PFBC Ashes

Table 10. Summary of the Properties of PFBC Ash-Based Synthetic Aggregate

Aggregate Properties*	No Lime Enhancement Karhula Ash	No Lime Enhancement Karhula Ash	Lime Enhancement Karhula Ash	Lime Enhancement Karhula Ash
Crush Strength, kg				
24 hours	10.4	12.3	146.6	54.9
48 hours	10.9	23.6	138.8	92.1
7 days	14.1	27.7	154.3	93.5
28 days	23.6	16.3	131.1	85.3
LA Abrasion Resistance				
Grade	B	B	B	B
Loss @ 28 days , %	75.29	89.14	26.07	38.9 (1)
Soundness**				
Loss after 5 cycles, %	27.97	14.06	-4.23	-7.80

* Curing conditions - 82°C (180°F) sealed for 24 hours.
** Magnesium sulfate solution.
na-not available
(1) Results from the 23 °C curing of the pelletized ash yield 19.22%. Excess moisture loss during curing at 82 °C is suspected

Pelletized Ash Properties The pelletized aggregate produced from Karhula PFBC ashes was tested according to ASTM procedures as they relate to its use in various construction applications. Pelletized ash from each of the pelletizing trials was tested for crush strength, Los Angeles abrasion resistance (ASTM C-131) and soundness (ASTM C-88).

The results of testing are presented in Table 10. The results indicate that without hydrated lime addition, the pelletized PFBC ash does not meet the ASTM or AASHTO construction aggregate requirements of a maximum of 40% weight loss. However, the addition of 5% hydrated lime results in compliance with these requirements for construction aggregate. In addition, the soundness of the aggregate using magnesium sulfate solutions was well below the AASHTO specifications of less than 18% loss after five cycles. In fact, the Karhula aggregate actually gained weight as a result of continued hydration during the five cycles.

Summary

The technical feasibility study examined the use of PFBC ash in construction-related applications, including its use as a cementing material in concrete and use in cement manufacturing, fill and embankment materials, soil stabilization, and synthetic aggregate production. In summary, PFBC ash represents a viable material for use in currently established construction applications for conventional coal combustion ashes.

PFBC ASH USE IN SOIL/MINE SPOIL AMENDMENT APPLICATIONS

PFBC ash use as a soil amendment for agricultural and reclamation activities represents a potentially large market. PFBC fly ash should be useful in soil/mine spoil amendment applications due of its high neutralization potential resulting from the $CaCO_3$. PFBC ash also can contain gypsum that precipitate aluminum and iron compounds from the soil solution in acid soil conditions, and supply nutrients, such as sulfur, potassium, and phosphorous, along with micronutrients that can benefit plant growth.

The study was initiated to address ash use options for PFBC fly ash in the agricultural and land reclamation industries. Specifically this study was to assess the use of PFBC fly ash to ameliorate acid soil and spoil materials. The research effort consisted of (1) a laboratory equilibration study to determine the influence of Karhula-low fly ash amendments on pH and EC of actively oxidizing acid-forming mine spoil; and (2) a greenhouse study that addressed germination and plant productivity for the Karhula ashes.

Ash Characteristics

The chemical characteristics of the PFBC fly ashes were evaluated to determine their potential for use to neutralize acidity and to provide nutritional value for plant growth. Saturated paste extracts were made using the method by Rhoades (1982). The method provided by Nelson (1982) was used to determine carbonates and gypsum. The acid-base potential determinations were made using evaluations specified in ASTM D 2492-77.

Fertility evaluations were determined using methods conducted at the Soil Testing Laboratory located at the Colorado State University. The elemental analyses were performed using inductively coupled plasma emission spectrometry (ICP) and ion chromatography (IC). Saturated paste extracts were conducted to determine the. availability of essential plant nutrients such as N, P, K, as well as a number of micronutrients. The results of these saturation paste extractions are shown in Table 11.

The levels of essential plant nutrients were found to be adequate, except for N. Fertilization of the treated spoil materials was performed to achieve equivalent levels for each treatment. The data show some potential problems such as a relatively high pH and EC values. These conditions could potentially have a negative effect on plant growth especially to salt and pH sensitive plants. However, once these materials are applied to the soil or spoil materials, dilution and the resulting environment may decrease their influence. These data also show that the PFBC fly ash can contribute significant amounts of essential plant nutrients to the spoil.

Table 11. Summary of the Chemical Characteristics of Extracts from the PFBC Ashes.

	Texas Acid Spoil	**Karhula-Low Fly Ash**	**Karhula-High Fly Ash**	**Karhula-High Bed Ash**
pH	2.3	10.4	11	12
EC (mS cm-1)	12	2.3	3.3	3.1
Organic Matter (wt. %)	3.6	0.1	0.3	0.6
AB-DTPA Extraction (mg L-1)				
NO3-N	2	3	9	1
P	0.6	29	3.7	3.4
K	0.2	64.8	50.1	29.4
Zn	16	3.3	4.0	1.0
Fe	553	46.3	39.7	50.4
Mn	10	2.3	9.3	31
Cu	2.6	1.2	1.4	0.3
Saturation Paste Extraction				
Ca (meq L-1)	23.6	26.8	35.9	29.4
Mg (meq L-1)	45.0	0.25	0.1	0.1
Na (meq L-1)	0.9	9.16	2.0	3.5
K (meq L-1)	1.56	1.02	0.2	0.7
SAR	0.15	2.5	0.5	0.9
Gypsum (meq L-1)	0	23.5	na	na
Neutralization Potential (t /(1000 t))	-24.4	138	148	527
Texture Estimate	Clay	Sandy Loam	Clay	Loamy Sand

na - not available

Laboratory Equilibration Study

Laboratory equilibration studies were conducted to address the use of PFBC ashes as amendments to ameliorated acidic spoil and soil conditions. The laboratory equilibration study was designed to determine the potential of the ash materials to neutralize the available acid and the potential acidity associated with oxidation of reduced materials present in the spoil. An acid spoil material from Texas was used for the study.

Humidity cells were used to simulate the oxidation of acid-forming soils under amended and non-treated conditions. Plastic containers were used as the humidity cells. The acidic spoil materials were spread in the containers to a depth of about 2.5 cm. The materials were initially wetted to field capacity and subjected to a series of 7-day cycles consisting of 3 days of dry air flowing over the materials followed by 3 days of saturated air and on day 7 the materials were saturated and allowed to equilibrate for 1 hour. Following the equilibration period, the solution was extracted from the spoil material and analyzed for pH and EC. The samples were allowed to dry at room temperature until the following day and the next 7-day cycle was initiated. The equilibration test was conducted for 8 cycles.

Ag-lime ($CaCO_3$) and Karhula fly ash were used as the soil neutralization amendment materials in the equilibrium humidity cell studies. The acid spoil material was treated with three levels of ag-lime and three levels of Karhula fly ash: (1) level 1 = 30.4 g ag-lime or 89.1 g Karhula fly ash/kg of spoil, based on acid-base potential, total S method ; (2) level 2 = 26.2 g ag-lime or 77.4 g Karhula fly ash/kg of spoil, based on acid-base potential, pyritic sulfur method multiplied by a mixing factor of 2; and (3) level 3 = 17.6 g ag-lime or 51.6 g Karhula fly ash/kg of spoil, based on acid-base potential, pyritic sulfur method with no mixing factor.

The neutralization potential of the PFBC fly ash applications were equivalent to the neutralization potential of the ag-lime materials at each level of application. Acidic materials with no neutralization amendment treatment were also used as a baseline case to show the further oxidation and resulting acidification of the acid soils under humidity cell conditions.

The humidity cell equilibration study showed the Karhula-low fly ash to be an effective acid neutralization amendment. The acid present in the treated materials was neutralized and the formation of acid from acid-forming minerals present in the spoil material was significantly reduced due to treatment with PFBC ashes. The pH and EC results associated with humidity cell weathering of the untreated, Karhula-low fly ash treated, and ag-lime ($CaCO_3$) treated acid spoil are presented in Figure 9.

The EC levels of the untreated spoil material increased substantially early on and then decreased. The large increase in EC values is directly attributable to the reaction products associated with the oxidation of pyritic materials in the spoil. The reduction of EC with time is associated with the removal of the oxidation products during the extraction process. Although the initial EC values are high, after about 14 days the solution in the system appears to be approaching equilibrium with the solid phase at an EC of about 5 mS/cm. These EC values were somewhat stable following each humidity cell cycle.

As expected, the spoil materials without treatment continued to oxidize. The pH changes were subtle, presumably due to the buffering of the system near pH 2.7. The ag-lime reacted almost immediately with the spoil material, increasing the pH to about 7.8 and maintaining it at that level over the 56 day test period. In general, the pH data for the Karhula-low amended spoil materials show the acid nature of the spoil material was neutralized by the Karhula fly ash. At time zero, the pH of the treated material was directly related to the amount of the fly ash applied. However, it is apparent that the reaction rate of the Karhula fly ash is slower than the ag-lime.

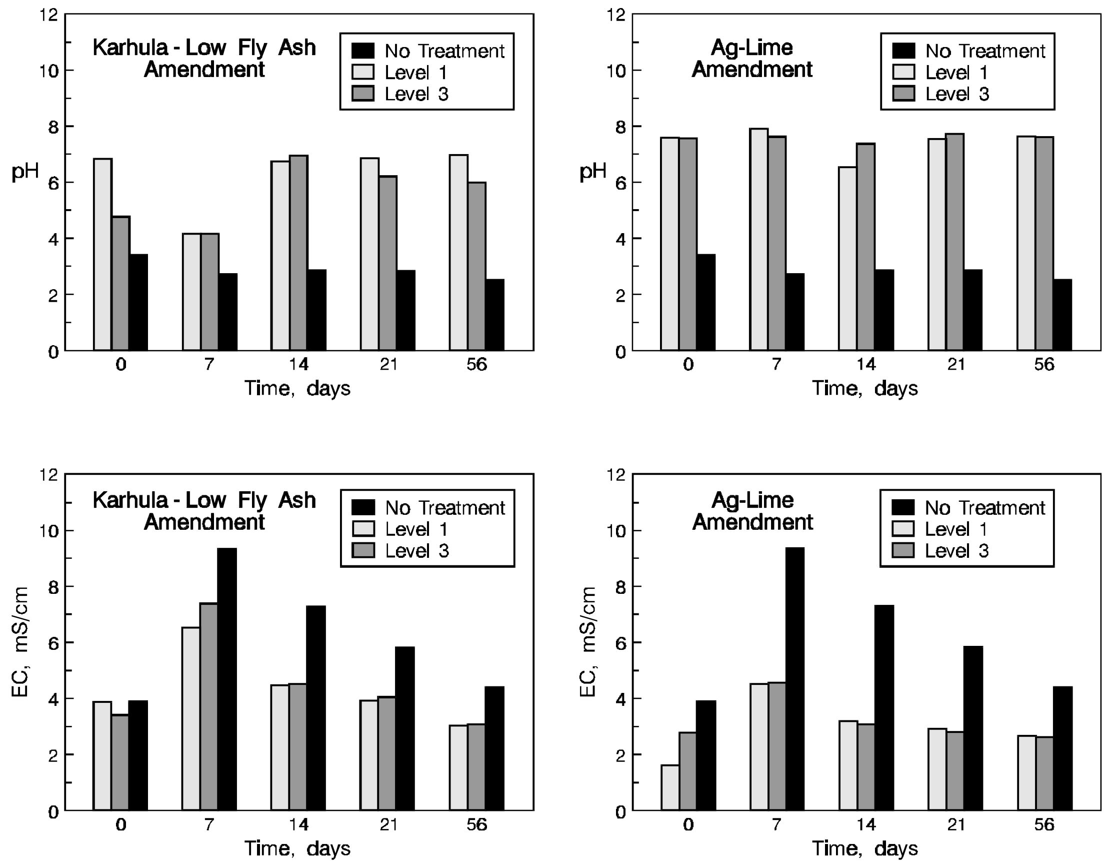


Figure 9. Influence of Ag-Lime and Karhula Fly Ash on Acidic Mine Spoil pH and EC

The data show a pH decrease of approximately 1 unit within the first 7 days. Apparently, the kinetics of acid generation of the spoil material was greater than the dissolution rate of the Karhula fly ash. After 14 days, the pH had risen to between 6 and 7, dependent upon the Karhula fly ash application rate and remained essentially constant through 56 days in the humidity cell.

Although the Karhula and ag-lime treated spoils were applied using equivalent neutralization potentials, the Karhula treated spoils exhibited a 1 unit lower pH than the ag-lime treated spoils. These types of differences can be attributed to the techniques by which the neutralization potential of fly ash materials are determined and the kinetics of the acid generation reactions.

The EC values associated with the ag-lime amended spoil material follows the same tendency as the untreated material with the increase in EC values to about 4.5 mS/cm at day 14, followed by a decrease and leveling to about 3.0 mS/cm with time. At day zero, the EC of each treated spoil is inversely related to the amount of amendment added. The reason for this relationship is not clearly understood. It seems that the largest ag-lime addition would result in the highest EC values, but the opposite was observed. These results could be associated with a reduction in the formation of acid due to the quantity of amendment added even though the pH values for each level of amendment addition are about the same.

The EC data for the Karhula treated acid spoil mirrors the behavior noted for the ag-lime treated acid spoil. The only notable difference is the slightly higher (1 mS/cm) EC values for the Karhula ash treatments than for the equivalent ag-lime treated spoils. The higher EC levels are associated with dissolution characteristics of the fly ash.

Though the humidity cell equilibration study showed the Karhula fly ash to be an effective acid neutralization amendment, there were several characteristics of the Karhula fly ash treated spoils materials that may have a potential to influence the successful use of the Karhula fly ash as an agronomic soil amendment. The lower early pH levels of approximately 4 for the Karhula fly ash treated spoils could cause some problems with germination and early plant growth with certain sensitive plant species. In addition, the Karhula fly ash treated spoils exhibited higher EC values, especially during the early phase of the humidity cell oxidation.

Greenhouse Productivity Studies

A greenhouse study was conducted to show the influence of PFBC ashes on the productivity of acidic mine spoil containing very high potential acidity. The study includes ashes from both Karhula tests and two vegetation types, specifically the Garrison Meadow Foxtail grass (*Alopecuras protensis cult. Garrison*) and the Common Bermuda grass (*Cynodon dactylon*). The study also addressed the germination of the species, which the laboratory equilibration study noted might be problematic.

The greenhouse study examined the Karhula-low and Karhula-high PFBC fly ashes, in addition to an ag-lime control. Karhula-high bed ash contains high levels of $CaCO_3$ and $CaSO_4$ and therefore was also included in the study. Garrison Meadow Foxtail grass and Common Bermuda grass are the production species. The duration of the greenhouse study was sufficient to allow for three cuttings of the grasses.

The experiment was placed on one bench in a greenhouse using a completely randomized designed replicated four time for each plant species.

Three levels of amendments were applied to the acid soils: (1) no application; (2) level 1 based on acid-base potential using the pyritic sulfur level: 21.05 g/kg ag-lime ($CaCO_3$), 85.5 g/kg Karhula-low fly ash, 142.23 g/kg Karhula-high fly ash and 39.9 g/kg Karhula-high bed ash; and (3) level 2 based on acid-base potential using total sulfur level: 31.6 g/kg ag-lime (CaCO3), 126.8 g/kg Karhula-low fly ash, 213.3 g/kg Karhula-high fly ash and 59.9 g/kg Karhula-high bed ash.

The greenhouse study was conducted under controlled conditions of light, temperature, fertilizer levels, and soil moisture requirements to maximize plant growth conditions. Fertilizer additions were based on nitrogen, phosphorous, and potassium levels and did not include concerns for nutrient ratios and micronutrient deficiencies.

Germination Tests The germination study involved the determination of the rate of germination for all three levels of amended spoil. Both the Meadow foxtail and the Common Bermuda grasses were used in the germination study. Exactly the same number of seeds (20) were planted in each pot and the number of plants that resulted were counted. The results are presented in Figure 10.

***Plant Productivity Tests* -** The results of the greenhouse plant productivity tests for the Meadow Foxtail and the Common Bermuda grass species are presented in Figure 11. The results clearly show that poor quality spoils can be successfully treated with PFBC ashes, resulting in good plant growth. It is very apparent that the untreated acid spoil was unable to support any plant growth as the seeds failed to germinate.

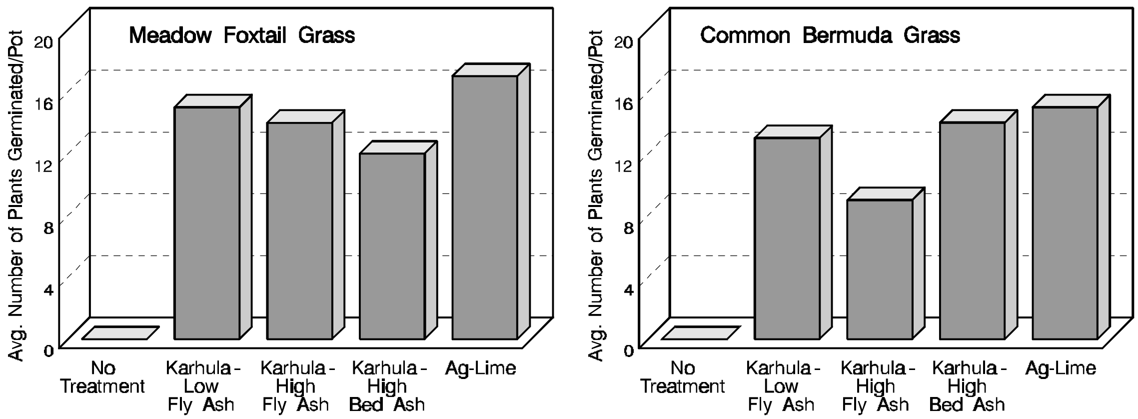


Figure 10. Germination Results of Grasses Grown on Karhula-Low Fly Ash, Karhula-High Fly Ash and Bed Ash, and Ag-Lime Amended Acidic Mine Spoil

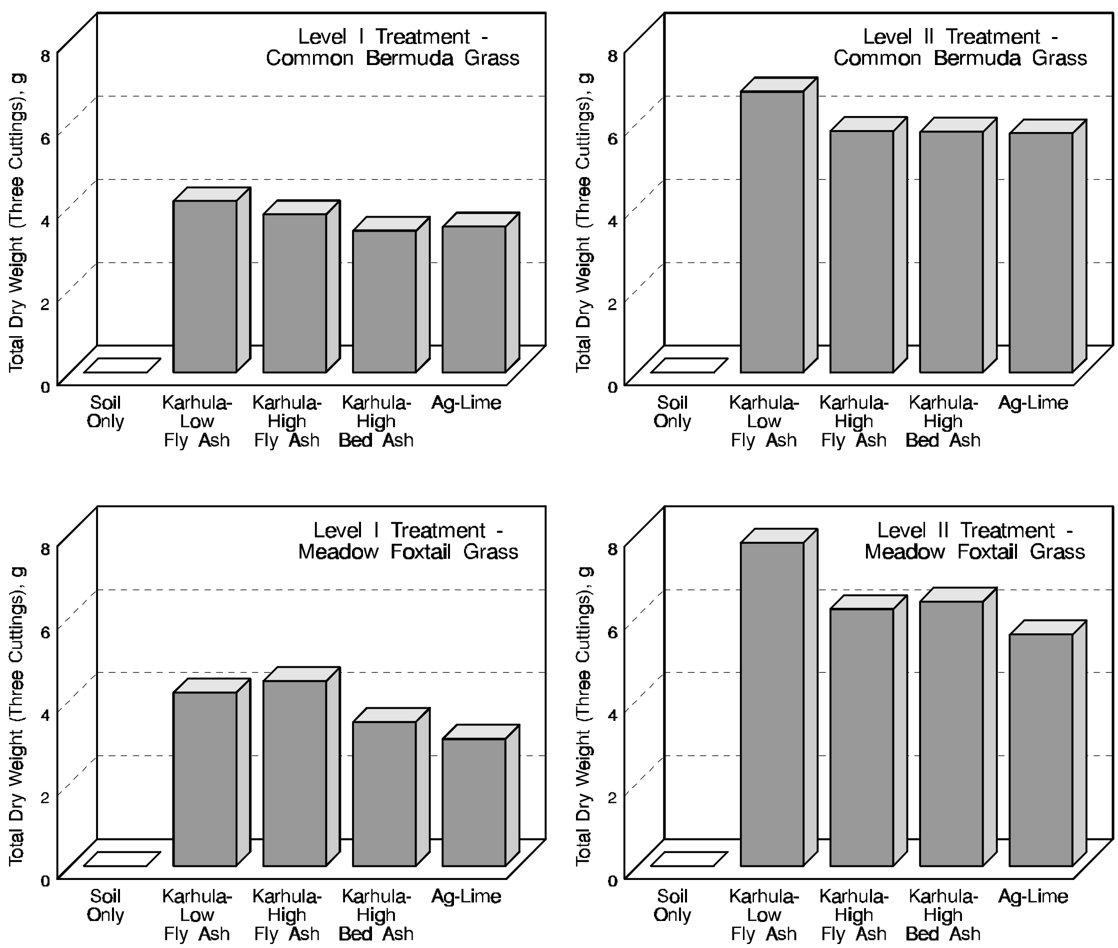


Figure 11. Dry Weight Production of Garrison Meadow Foxtail Grass and Bermuda Grass Grown on Karhula-Low Fly Ash, Karhula-High Fly Ash and Bed Ash, and Ag-Lime Amended Acidic Mine Spoil

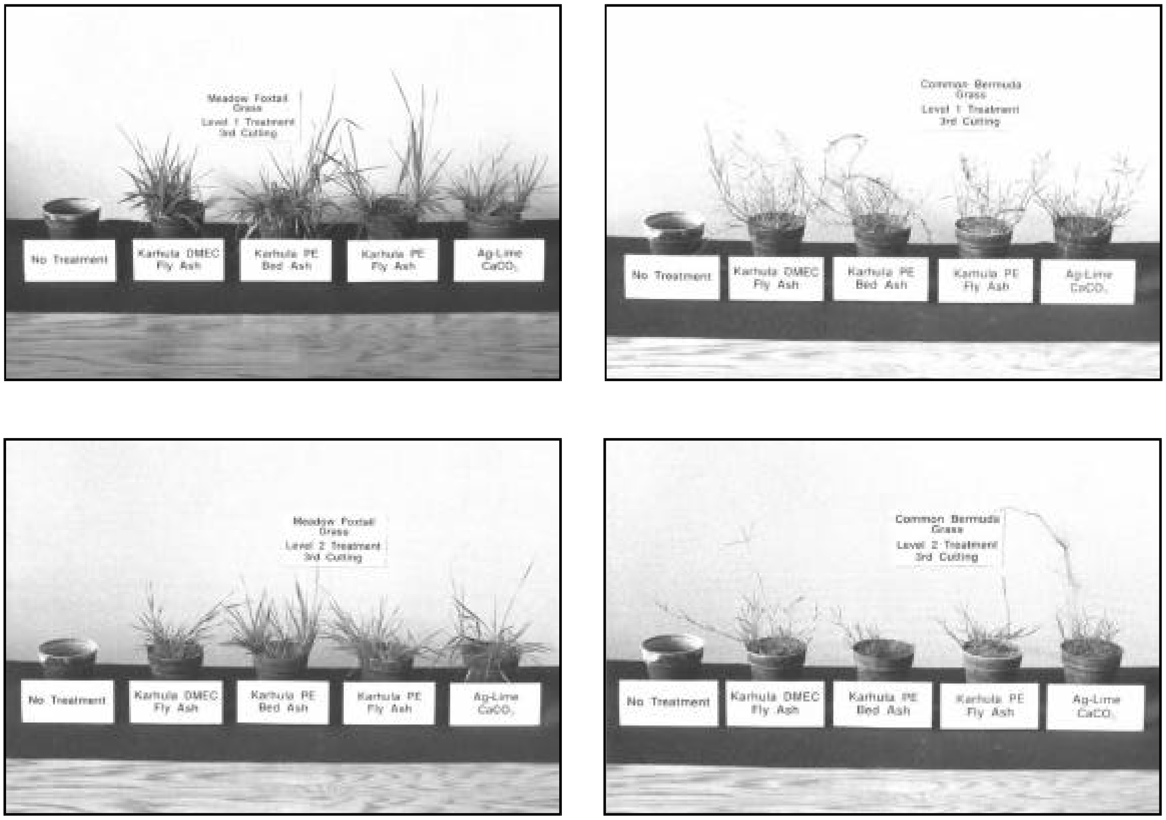


Figure 12. Photograph of the Production of Meadow Foxtail Grass and Common Bermuda Grass Grown on Ag-Lime, Karhula-Low Fly Ash (Karhula DMEC), and Karhula-High Fly Ash (Karhula PE) and Bed Ash Amended Mine Spoil (Level 1 and Level 2)

The results show PFBC ashes to be more effective than ag-lime in plant production and root penetration. Total plant production for the three cuttings was higher for the Karhula-low fly ash treatments compared to the ag-lime treatment at the lower amendment application level (level 1). At the higher amendment application rate (level 2), the Karhula-low fly ash treatment resulted in higher plant production compared to the ag-lime treatments, which were comparable with the Karhula-high fly ash and bed ash treatments.

Photographs showing the plants at the time of the third cutting for acid spoils amended with the PFBC ashes, ag-lime and no treatment conditions are presented in Figure 12. These results were somewhat unexpected based on the more beneficial pH and EC conditions associated with the ag-lime amended spoil.

The findings of this study are probably due to the nutritional issues associated with micronutrients rather than to pH and EC conditions. However, an obvious factor responsible for the differences in the plant production between the Karhula-low fly ash amended spoil was the root penetration. The Karhula-low fly ash treated spoils contained root matter throughout the potted spoil, while much of the root mass in the ag-lime treated soil was associated with the sides of the pots. These data clearly show that PFBC ashes are at least effective as ag-lime for the reclamation of acid soils and spoils.

In summary the greenhouse studies show the PFBC ashes to be as effective as ag-lime in promoting seed germination and in promoting plant production and root penetration.

Summary

The technical feasibility study examined the technical feasibility of PFBC ash as a soil amendment for acidic soils and spoils encountered in agricultural and reclamation applications. In summary, PFBC ash represents a viable material for use in currently established mining and soil amendment applications for conventional coal combustion ashes.

SUMMARY AND CONCLUSIONS

Western Research Institute, in conjunction with the Electric Power Research Institute, Foster Wheeler International, Inc. and the U.S. Department of Energy, has undertaken a research and demonstration program designed to examine the market potential and the technical feasibility of ash use options for PFBC ashes. Ashes from the Foster Wheeeler Energia Oy pilot-scale circulating PFBC tests in Karhula, Finland, combusting (1) low-sulfur subbituminous and (2) high-sulfur bituminous coal were evaluated in laboratory and pilot-scale ash use testing at WRI.

PFBC Ash Use In Construction Applications

The technical feasibility study examined the use of PFBC ash in construction-related applications, including its use as a cementing material in concrete and use in cement manufacturing, fill and embankment materials, soil stabilization agent, and use in synthetic aggregate production. The results of the technical feasibility testing indicated the following:

- PFBC ash does not meet the chemical requirements as a pozzolan for cement replacement. However, it does appear that potential may exist for its use in cement production as a pozzolan and/or as a set retardant.
- PFBC ash shows relatively high strength development, low expansion, and low permeability properties that make its use in fills and embankments promising.
- Testing has also indicated that PFBC ash, when mixed with low amounts of lime, develops high strengths, suitable for soil stabilization applications and synthetic aggregate production. Synthetic aggregate produced from PFBC ash is capable of meeting ASTM/AASHTO specifications for many construction applications.

PFBC Ash as a Soil/Mine Spoil Amendment

The technical feasibility study examined the technical feasibility of PFBC ash as a soil amendment for acidic problem soils and spoils encountered in agricultural and reclamation applications. The results of the technical feasibility testing indicated the following:

- PFBC fly ashes were effective acid spoil and sodic spoil amendments. In a comparison with ag-lime, the fly ashes reacted with the acidic spoil at a slower rate and the final pH of the treated material was slightly lower (i.e., fly ash treated, pH $\cong$ 7 and the ag-lime treated $\cong$ 8). EC values of the fly ash treated spoils were about 1 mS/cm higher than the EC values associated with the ag-lime treated materials.

- The greenhouse studies demonstrated that PFBC fly ash amended spoils resulted in higher plant productivity than the ag-lime amended spoils. These results possibly are due to pH and nutritional issues, but root penetration was undoubtedly a factor.

In conclusion, there is a significant market potential for PFBC ash in the construction and soil amendment industries. In particular, PFBC ash represents a technically viable material for use in these currently established applications for conventional coal combustion ashes. The chemistry of the PFBC ashes directly controls the geotechnical properties of the PFBC ash in reuse options. It is possible to modify the hydration reaction chemistry of the PFBC ashes through such processes as lime enhancement to produce the geotechnical properties required for construction applications. As a result, PFBC ash should be viewed as a valuable resource, and commercial opportunities for these materials should be explored for future PFBC installations.

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